Atmospheric Reactivity Research on Selected Pesticides

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May 22, 2007

Outline

- Background: VOCs, air quality, and reactivity
- Types of pesticide VOCs of interest for reactivity research
- UCR pesticide reactivity research project: objectives, methods, and results
- Estimated relative O_3 and PM impacts of pesticide VOCs
- Conclusions

VOCs and Air Quality

- Volatile Organic Compounds (VOCs) enter the atmosphere from a variety of anthropogenic and biogenic sources
- Impacts of VOCs on air quality include:
  - Direct effects (for toxic VOCs very near large sources)
  - Formation of toxic or persistent oxidation products
  - Promotion of ground-level ozone formation
  - Contribution to secondary particle matter (PM) formation
- Contribution to ground-level ozone has been the major factor driving VOC regulations in the U.S.
  - Models calculate large VOC reductions are needed to achieve air quality standards in urban areas
  - NO_x reduction is more important to reducing regional ozone
- But need to reduce PM is also a priority. Secondary Organic Aerosol (SOA) from reactions of VOCs contributes to fine PM.

Mechanism of VOCs Impact on O_3

- Ground level O_3 is actually formed from the photolysis of NO_2, with O_3 in a photostationary state relation with NO and NO_2:

$$NO_2 + h\nu \rightarrow O(^3P) + NO$$
$$O(^3P) + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow O_2 + NO_2$$

Overall:

$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} O_3 + NO$$

- VOCs promote O_3 by forming radicals that convert NO to NO_2 and shift the photostationary state towards O_3 formation, e.g.:

$$RH + OH \rightarrow H_2O + R\bullet$$
$$R\bullet + O_2 \rightarrow RO_2\bullet$$
$$RO_2\bullet + NO \rightarrow RO\bullet + NO_2$$
$$RO\bullet \rightarrow \rightarrow HO_2 + \text{other products}$$
$$HO_2 + NO \rightarrow OH + NO_2$$

Overall:

$$VOC + O_2 \overset{h\nu,\ NO_x,\ O_2}{\rightarrow\ \rightarrow\ \rightarrow} O_3 + \text{products}$$

Factors Affecting Impacts of VOCs on O_3

- Ground level O_3 is formed from the reactions of NO_x. But without VOCs O_3 levels are low because of its reaction with NO.
- VOCs differ significantly in their effects on O_3 formation Mechanistic factors affecting ozone impacts are:
  - How fast the VOC reacts
  - NO to NO_2 conversions caused by VOC's reactions
  - Effect of reactions of VOC or its products on radical levels
  - Effects of reactions of VOC or its products on NO_x levels
- The effect of a VOC on O_3 also depends on where it reacts
  - The availability of NO_x. (NO_x necessary for O_3 to form.)
  - The amount of time the VOCs have to react
  - The sensitivity to radical levels
- Models must take these factors into account to evaluate effective VOC control strategies to reduce O_3.

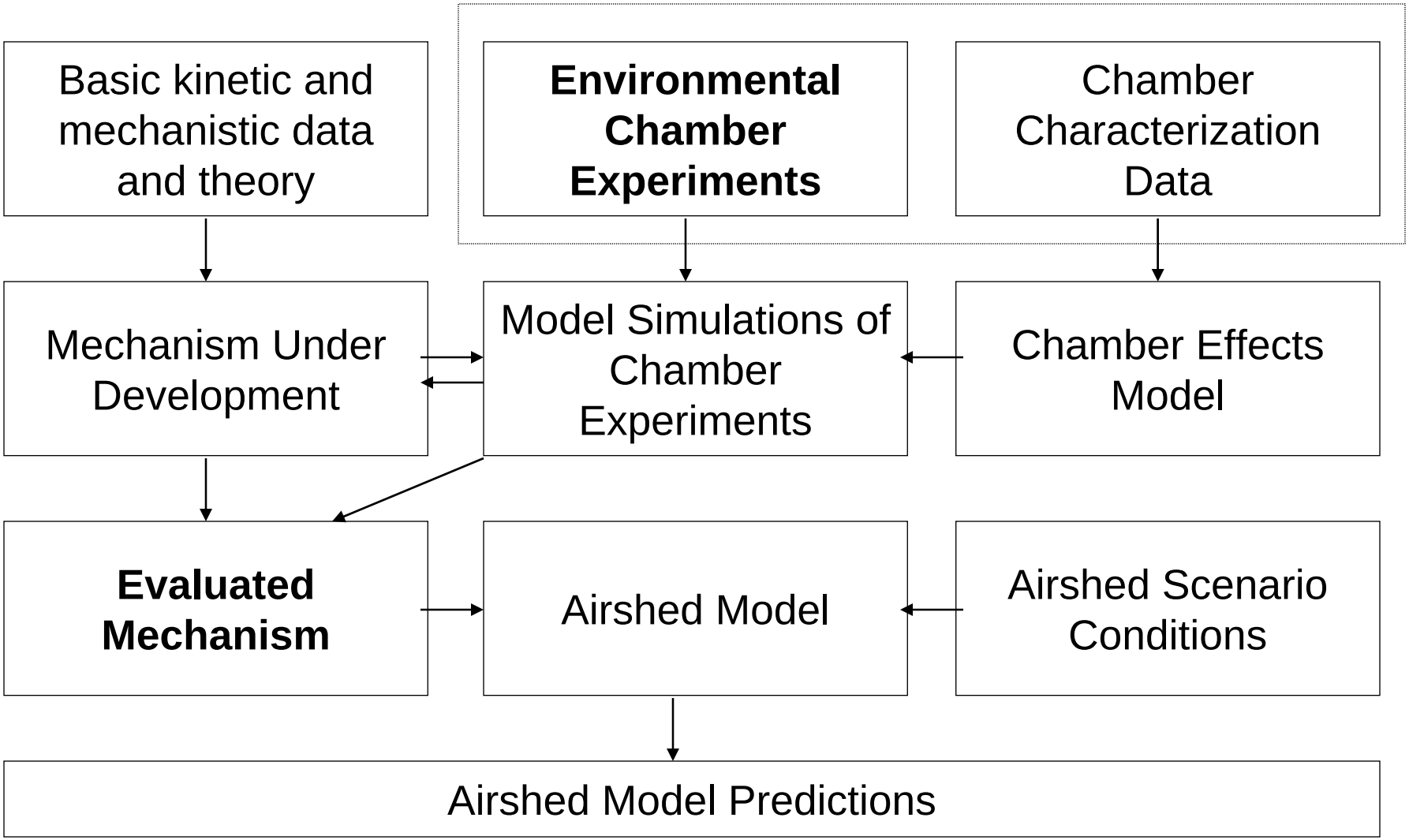
Factors Affecting Impacts of VOCs on Secondary PM

- Many VOCs form low volatility oxidation products that can partition into the aerosol phase and contribute to secondary PM
- Some higher volatility products may also partition into the aerosol phase due to heterogeneous reactions
- The yields of condensable products varies from compound to compound and may also vary with atmospheric conditions
- Identity, yields, formation mechanisms, and partitioning coefficients of condensable products are mostly unknown for most VOCs
- Data and mechanistic knowledge are inadequate for models to predict secondary PM from VOCs with any degree of reliability.
- Inadequately tested and highly simplified parameterized models are used for predicting effects of emissions on secondary PM

Importance of Environmental Chamber Data to Air Pollution Models

- **Chemical mechanisms** are needed for models to predict effects of VOCs on secondary pollutants such as O_3 and PM
- Mechanisms in current airshed models have many uncertain estimates, simplifications and approximations
- **Environmental chambers**, simulating atmospheric reactions under controlled conditions, are essential to:
  - Develop predictive mechanisms when basic mechanistic data insufficient.
  - Testing approximations and estimates in mechanisms for almost all VOCs under simulated atmospheric conditions
  - Testing entire mechanisms under the necessary range of conditions
- Results of experiments are influenced by chamber effects, so developing an appropriate chamber effects model is important

Relationship Between Mechanisms, Chamber Data and Airshed Models



UCR Project to Investigate Atmospheric Reactivities of Selected Pesticide VOCs

Background

- Data are not available concerning O_3 and PM impacts for many types of pesticide VOCs used in California. Therefore, estimates of these impacts are very uncertain

Objectives

- Reduce uncertainties in estimates of O_3 impacts for pesticides used in California
- Obtain qualitative information on relative PM impacts or representative pesticide VOCs
- Make recommendations on how to represent pesticide VOCs in airshed models

UCR Project to Investigate Atmospheric Reactivities of Selected Pesticide VOCs

Approach

- Assess available information and select representative pesticide-related compounds most in need of study
- Conduct environmental chamber experiments to develop mechanisms for predicting O_3 impacts of the studied compounds
- Incorporate mechanisms for these and related compounds into the overall mechanism used to predict ozone impacts of VOCs.
- Derive ozone impacts of the pesticides in various O_3 reactivity scales, including the MIR scale used in California regulations
- Obtain data on relative PM impacts of the studied compounds, and compare them with other compounds studied previously

Volatile Compounds in Pesticide Profile in 2000 California VOC Emissions Inventory

Compound	Wt. %	Structure	Comments
Methyl Bromide	25%	CH_3Br	Very low reaction rate
Methyl Isothiocyanate	18%	CH_3NCS	No mechanism. Reaction rate known
1,3-Dichloropropenes	11%	$ClCH=CHCH_2Cl$	Some mechanistic data available
Chloropicrin	9%	CCl_3NO_2	Previously studied
Aromatic 200 Solvent	5%	Aromatic Mixture	Accuracy of existing mechanism uncertain
Xylene Solvent	5%	xylene isomers	Previously studied
Various Thiocarbamates	~4%	Compounds with >NC(O)S- group	Some kinetic and mechanistic data available

Volatile Compounds in Pesticide Profile in 2000 California VOC Emissions Inventory

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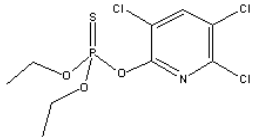
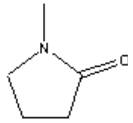
Compound	Wt. %	Structure	Comments
Kerosene	2%	Hydrocarbon mixture	Some data on lighter mixtures
Chlorpyrifos	2%		Volatility too low to study (vp ~30 ppt)
Methy isobutyl ketone	1%	$CH_3C(O)CH_2CH(CH_3)CH_3$	Previously studied
Acrolein	0.7%	CH_2=CHCHO	Previously studied
Glycerine	0.5%	$HOCH_2CH(OH)CH_2OH$	Mechanism can be estimated
Propylene Glycol	0.5%	$CH_3CH(OH)CH_2OH$	Previously studied
N-methyl pyrrolidinone	0.5%		Previously studied

Pesticide Related VOCs Chosen for Study

Methyl Isothiocyanate

- Highest emissions in profile with non-negligible reaction rate.
- No mechanisms have been derived or evaluated for isothiocyanates.

1,3-Dichloropropenes

- 2nd highest in profile with non-negligible reaction rate.
- Mechanisms of halogenated compounds are uncertain

EPTC (S-ethyl N,N-di-n-propyl thiocarbamate)

- Chosen as a representative thiocarbamate.
- Some kinetic and mechanistic data available, but no data to evaluate mechanisms for thiocarbamates

continued ...

Pesticide Related VOCs Chosen for Study
(continued)

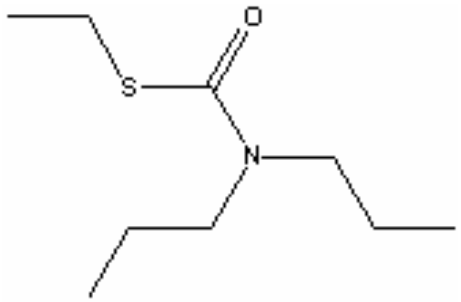
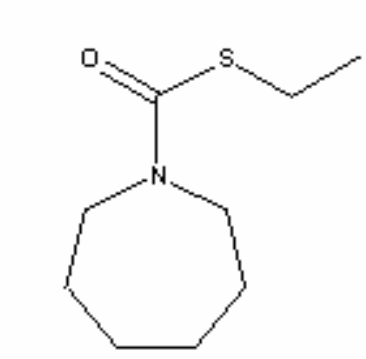
Kerosene

- Highest emissions in profile of hydrocarbon solvents
- Complex mixture of C_8-C_{18} alkanes (82%) and aromatics (18%)
- Data available to test mechanisms for “mineral spirits” and other hydrocarbon solvents used in coatings, but not kerosene.
- Mechanism derived based on speciation data provided by ExxonMobil Process Laboratories in Baton Rouge, LA

Carbon Disulfide (CS_2)

- Known to be important as a pesticide breakdown product
- Kinetic and mechanistic data available, but no data available to evaluate mechanisms for ozone and PM impacts.

Thiocarbamate Pesticides

EPTC (0.5%)	Molinate (3.3%)
	
Representative compound chosen for study Mechanism derived and evaluated using results of experiments for this project	Being phased out so priority for study reduced Mechanism estimated based on mechanism derived for EPTC

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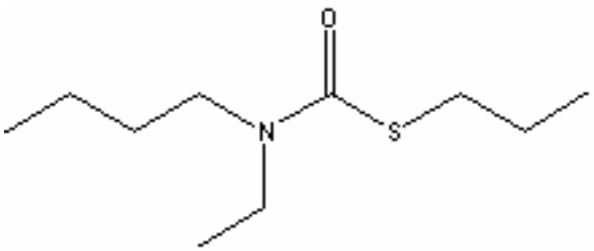
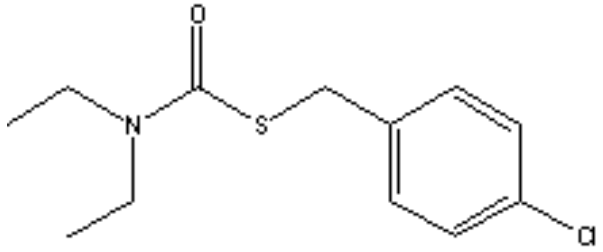
Thiocarbamate Pesticides (continued)

Pebulate (0.4%)	**Thiobencarb (0.5%)**
	
Mechanism estimated based on mechanism derived for EPTC	Mechanism estimated based on mechanisms derived for EPTC and toluene

Environmental Chamber Experiments

Purpose

- Provide data to test ability of mechanisms to predict O_3 impacts
- Obtain qualitative information on relative PM impacts
- Obtain data on relevant VOC rate constants, where needed

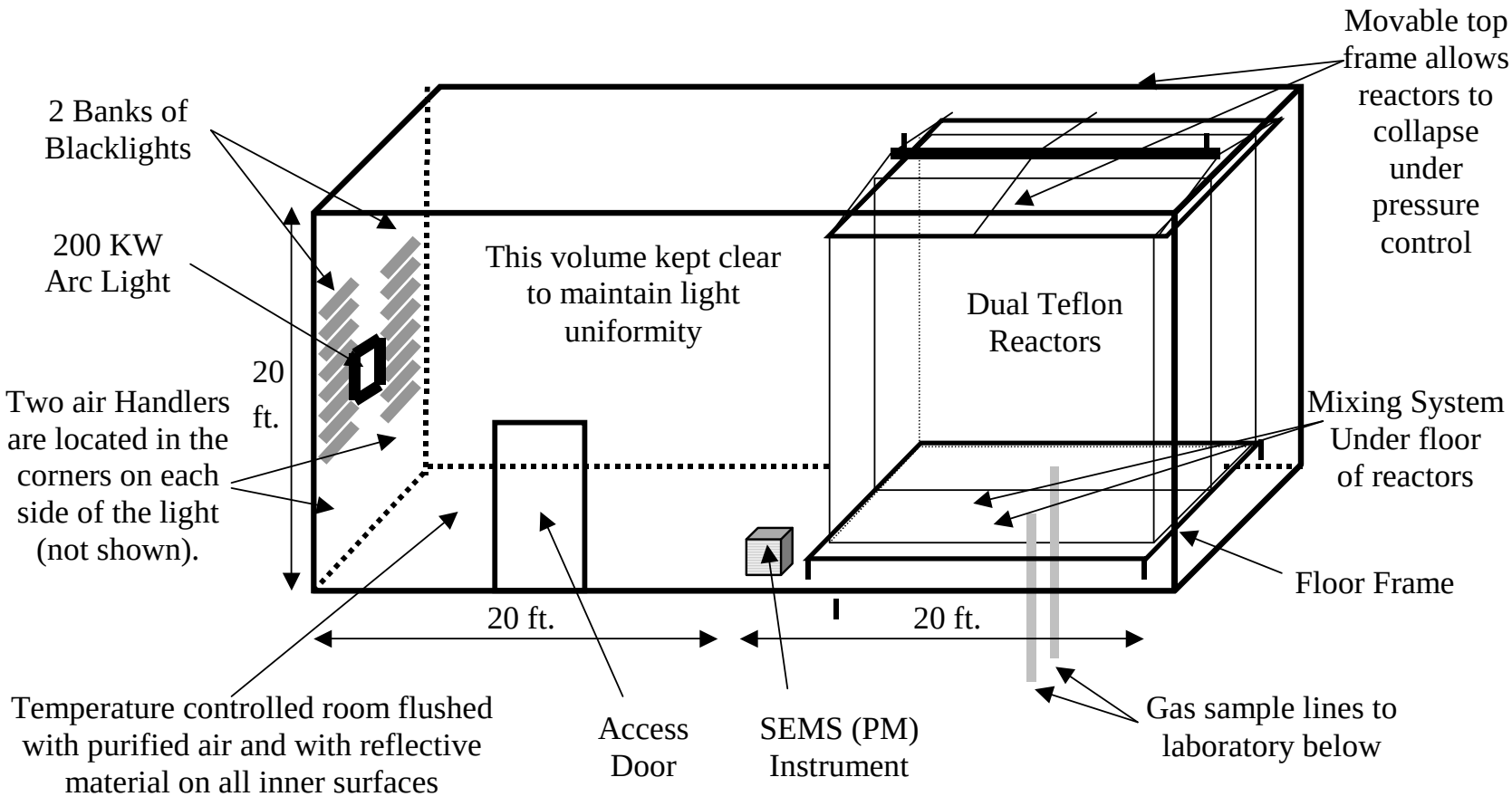
Types of Experiments

- Incremental reactivity experiments: Add test compound to reactive organic gas (ROG) surrogate - NO_x irradiations simulating ambient conditions
- Single VOC - NO_x irradiations where useful
- UCR EPA chamber (with blacklight light source) employed

Characteristics of New UCR EPA Chamber

- Indoor chamber design used for maximum control and characterization of conditions
- Dual reactor design for experimental productivity and to simplify reactivity assessment
- Largest practical volume for indoors (two ~100,000-L reactors)
- Blacklights or argon arc solar simulator light sources
- Teflon reactors in “clean room” to minimize background
- Positive pressure reactor volume control to minimize contamination
- Temperature controlled to ±1^{o}C in ~5^{o}C to ~50^{o}C range.
- Large array of analytical instrumentation
- Instrumentation for monitoring PM formation

Diagram of UCR EPA Chamber



Photographs of Chamber and Lights

Looking Towards Reactors (from light)

Looking Towards Lights and Air Inlet

Chemical Mechanism Development

SAPRC-99 chemical mechanism used as starting point

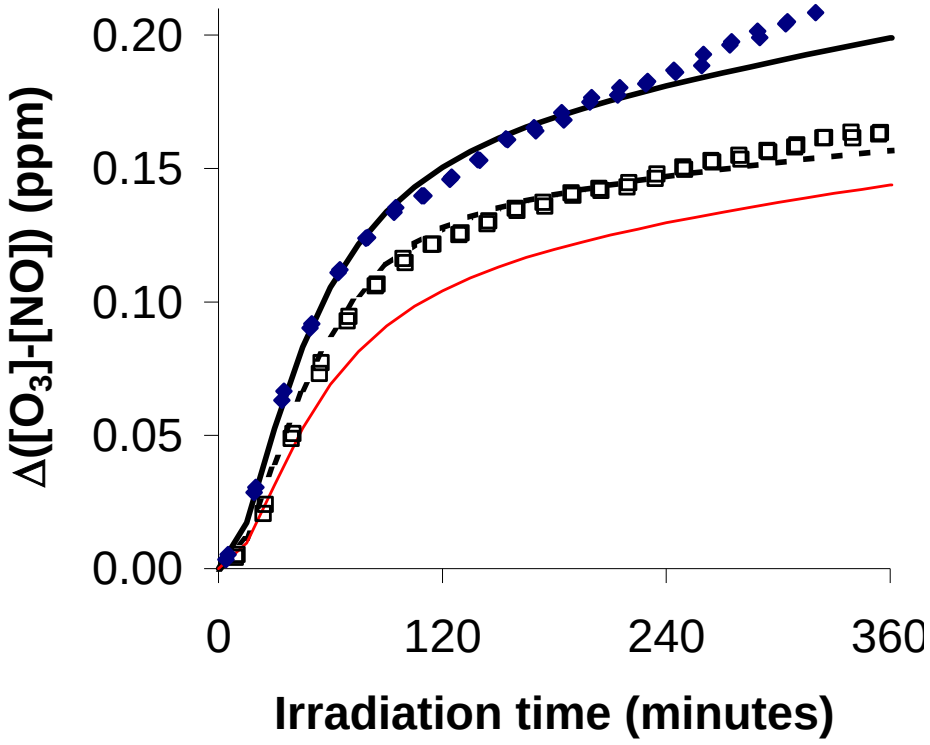
- Used in airshed models to calculate reactions of emitted VOCs and their impacts on O_3 and other pollutants
- Used to calculate O_3 reactivity scales for ~800 types of VOCs, including the MIR scale used in CARB's reactivity regulations
- Did not previously include reactions for the representative pesticide VOCs chosen for study

Pesticide VOC reactions added to SAPRC-99 mechanism

- Preliminary mechanisms derived for the pesticide VOCs based on available literature data and estimates
- Mechanisms refined and adjusted as needed based on results of experiments for this project

Results of Selected Experiments

EPA589: Surrogate + MITC

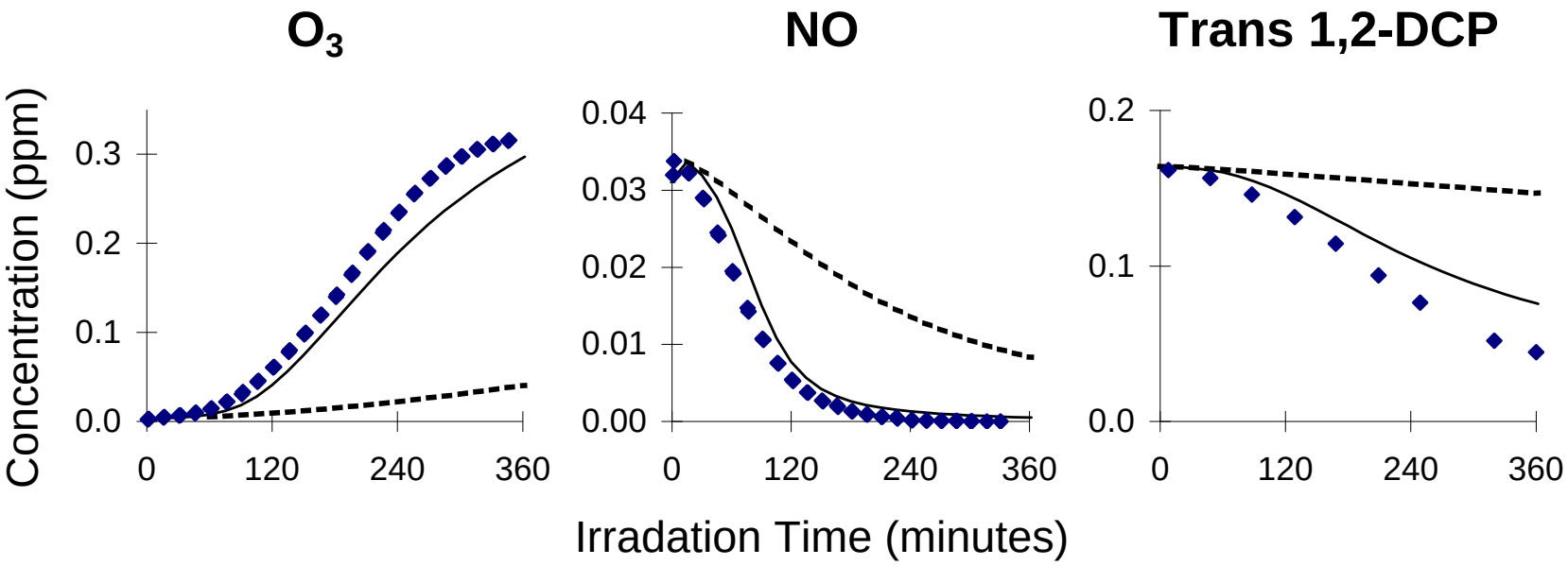


- Base Experiment (25 ppb NOx, 1 ppmC ROG surrogate)
- Model simulation of Base Case Experiment
- Experiment with 1 ppm MITC added
- Model simulation of test experiment (Mechanism "A")
- Model simulation of test experiment (Mechanism "B")

- **Mechanism A: Major fate of HSO in experiment is HSO + O_2**
- **Mechanism B: Major fate of HSO in experiment is HSO + NO_2**

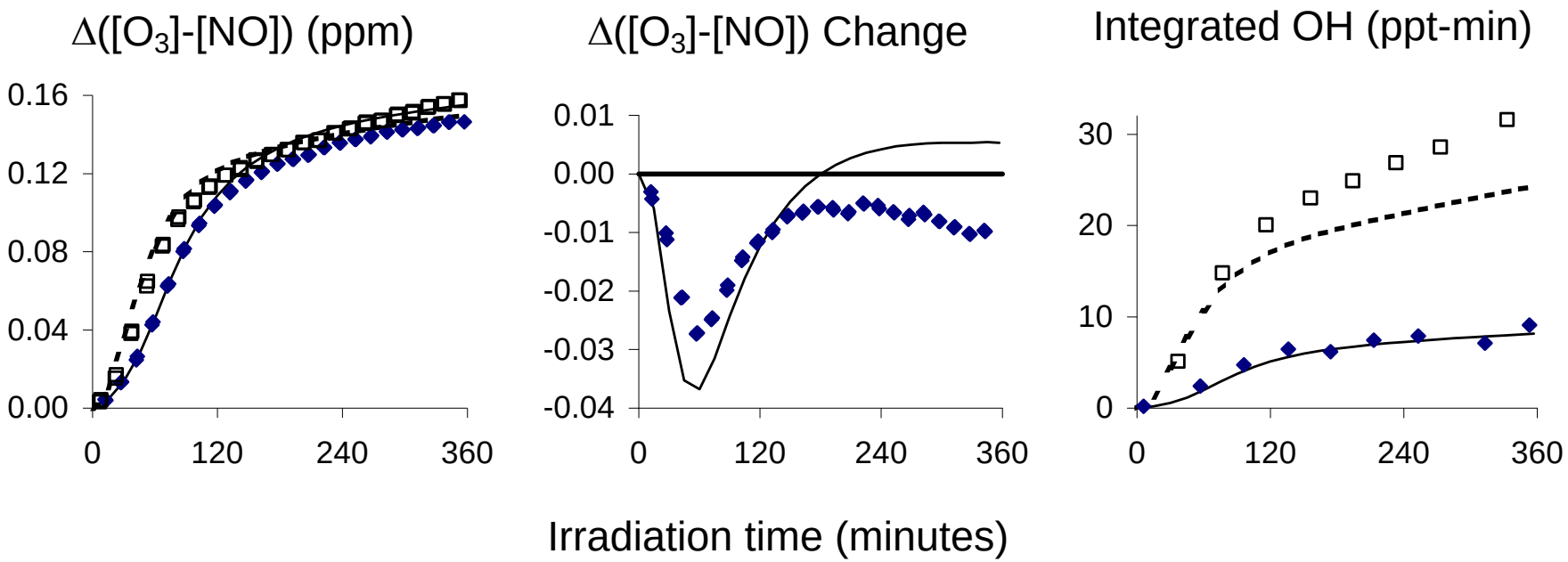
Results of Selected Experiments (continued)

EPA551B: 0.4 ppm 1,3-Dichloropropenes + 50 ppb NOx



Results of Selected Experiments (continued)

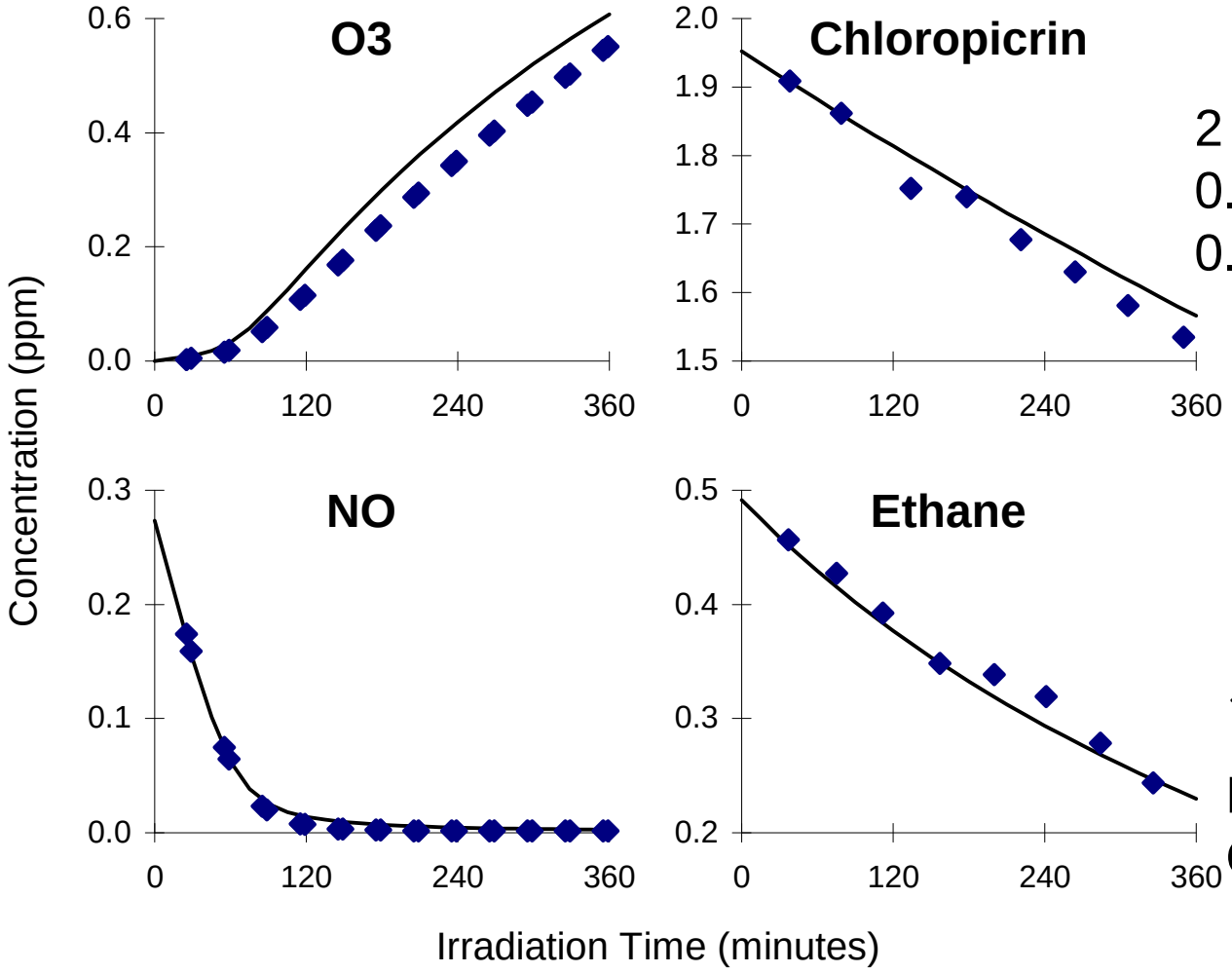
EPA590: Surrogate + EPTC



- ▫ Base Experiment (25 ppb NOx, 1 ppmC ROG surrogate)
- - - Model simulation of base experiment
- ◆ Experiment with 0.25 ppm EPTC added
- —— Model simulation of added EPTC experiment

Results of Selected Chloropicrin Experiment

(Carried out for a previous project)



CTC134A

2 ppm Chloropicrin
0.4 ppm NOx
0.5 ppm ethane

◆ Experimental

— Model

Ethane is tracer for Cl atom formation

Mechanism Development Results

Mechanisms were derived for MITC, EPTC, and CS_2 that were consistent with the chamber results

- Data used to obtain rate constants for OH + MITC and to refine the rate constant for OH + EPTC
- Uncertain aspects of mechanisms for MITC, EPTC, and CS_2 had to be adjusted to satisfactorily simulate the chamber data
- Mechanism derived for EPTC were used to derive estimated mechanisms for molinate, pebulate, and thiobencarb,

The model for Kerosene based on analysis by ExxonMobil gave satisfactory simulation of the chamber results

continued ...

Mechanism Development Results (continued)

Mechanisms were derived for the 1,3-dichloropropenes and chloropicrin that were consistent with chamber results

- Chlorine chemistry was added to the SAPRC-99 mechanisms to permit representation of these chlorine-containing compounds
- It is necessary to explicitly represent chloroacetaldehyde to correctly simulate dichloropropene reactivity. This has implications for mechanisms for chlorinated VOCs in general.
- An updated mechanism for chloropicrin developed and found to give good simulations of experiments carried out previously.

The mechanisms developed for these pesticide compounds are being incorporated in the updated SAPRC-07 mechanism that is nearing completion

Ozone Reactivity Scales

Incremental reactivity scales provide a means to quantify relative differences among VOCs in their O_3 impacts

$$\text{Incremental Reactivity of VOC} = \frac{O_3 \text{ formed when VOC added to the scenario} - O_3 \text{ formed in model of an ambient scenario}}{\text{Amount of VOC Added}}$$

Incremental reactivities depend on ambient conditions. Different scales can be derived to represent different types of conditions

- MIR scale: Conditions where O_3 is most sensitive to VOCs
- EBIR scale: Conditions where O_3 is equally sensitive to VOCs and NOx

The CARB uses the MIR scale in several reactivity-based VOC regulations

Representative MIR and EBIR Reactivities

Compound or Mixture	O_3 Reactivity (Mass Basis)	
	MIR	EBIR
Ambient Emissions Mixture	3.6	0.8
1,3-Dichloropropenes	4.3	0.9
Chloropicrin	1.9	1.2
EPTC	1.6	0.5
Kerosene	1.5	0.3
MITC	0.3	0.2
Ethane *	0.3	0.13
Carbon Disulfide	0.2	0.13
Methyl Bromide	0.02	0.01

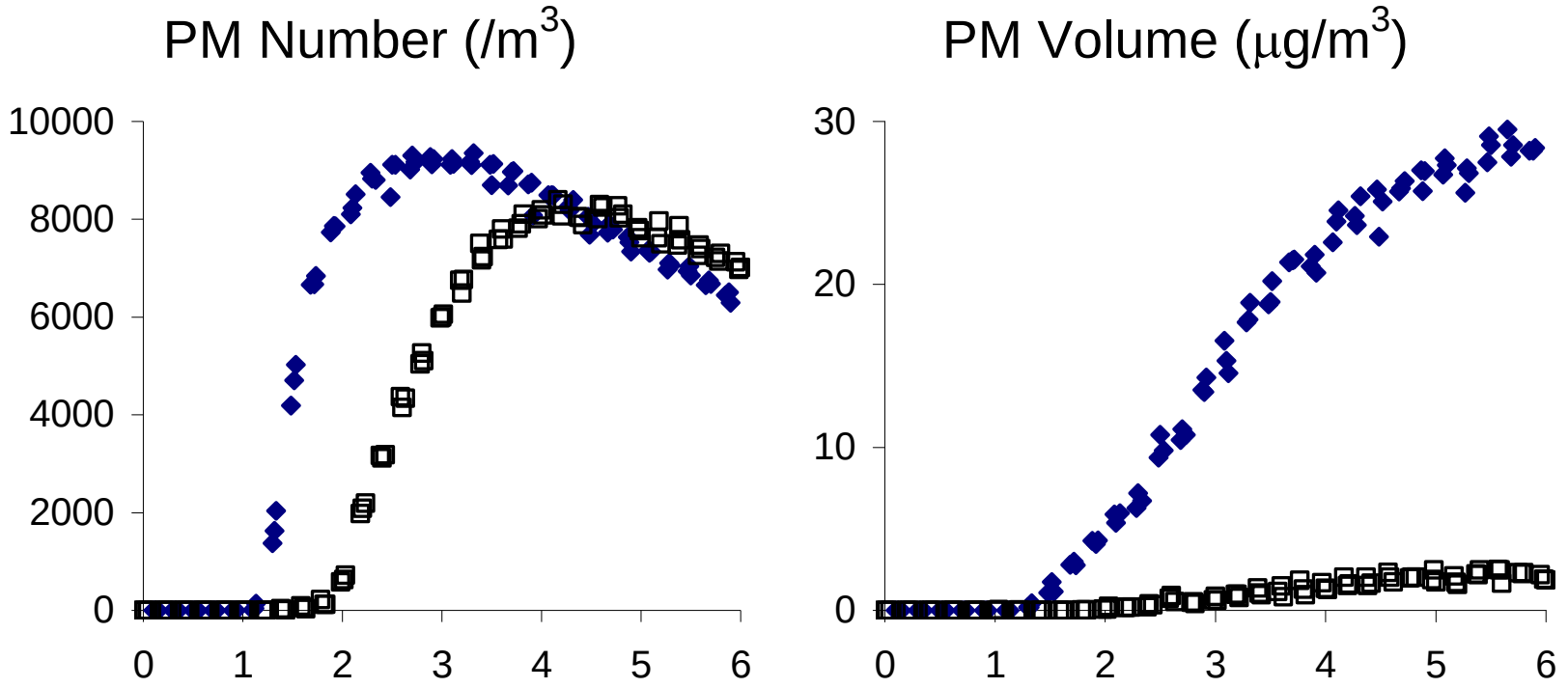
Calculated using new SAPRC-07 Mechanism

* Used by the EPA as the standard to define “negligible” reactivity

PM Measurements in the UCR EPA Chamber

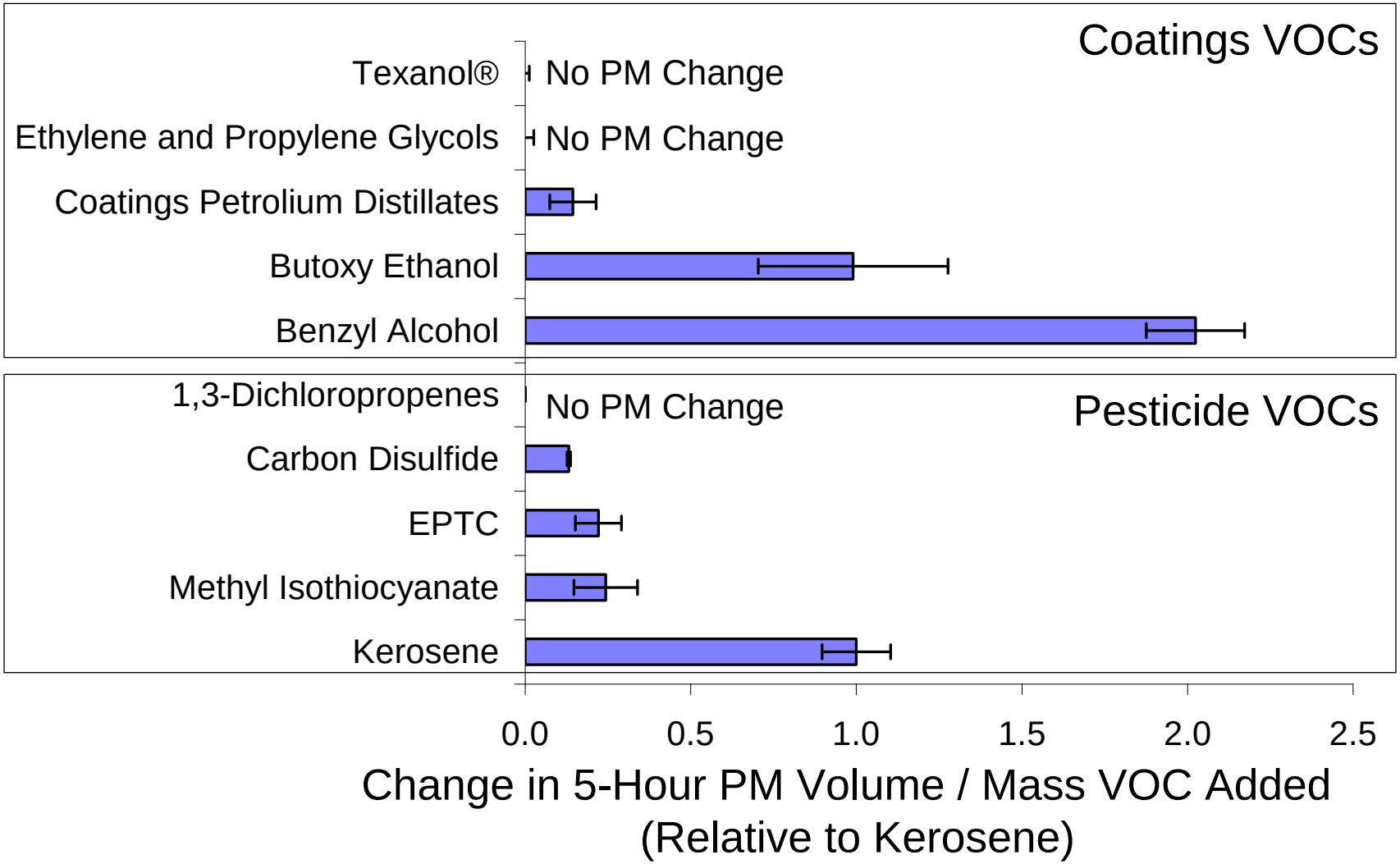
- PM Measurements are being made in conjunction with most UCR EPA chamber experiments. PM alternately sampled from each of the two reactors, switching every 10 minutes
- Number densities of particles in 71 size ranges (28 - 730 nm) measured using a a Scanning Electrical Mobility Spectrometer. Data used to compute particle number and volume densities
- Background PM formation now less than 0.5 $\mu g/m^3$. (Was up to 2 $\mu g/m^3$ in Reactor A before it was replaced)
- Most experiments to date are unhumidified with no seed aerosol
- PM measurements made during reactivity experiments with representative architectural coatings and pesticide VOCs.

Representative PM Data



- Base Experiment (30 ppb NOx, 0.6 ppmC Base ROG)
- 1.5 ppmC Kerosene Added

Relative PM Formation In Surrogate - NOx + Test VOC Experiments



Conclusions

- Uncertainties in estimates of O_3 impacts of important types of pesticides used in California have been reduced
- Information has been obtained to improve O_3 impact estimates for Sulfur- and Chlorine-containing compounds in general
- Pesticide reactivities have been added to reactivity scales that can be used for regulatory applications
- Information has been obtained concerning differences in PM impacts of representative pesticides
- Uncertainties remain in mechanisms for many types of VOCs
- Improved mechanisms and data are needed to *quantitatively* predict PM impacts in models
- Air quality impacts of very low volatility pesticides are uncertain

Acknowledgements

- **Irina Malkina, Kurt Bumiller, Bethany Warren**
  - Major effort in conducting pesticide chamber experiments
- **David Cocker**
  - Overall guidance for PM studies
- **Dennis Fitz, Kurt Bumiller, Claudia Sauer, John Pisano, Charles Bufalino, Matthew Smith**
  - Assistance in design and construction of UCR EPA Chamber
- **California Air Resources Board**
  - Funding source for pesticide reactivity and mechanism development projects
- **United States Environmental Protection Agency and South Coast Air Quality Management District**
  - Funding sources for chamber construction and for PM studies on coatings VOCs, respectively